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On the Origin of Microheterogeneity: A Mass Spectrometric Study of Dimethyl Sulfoxide−Water Binary Mixture

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We have studied the microscopic solvent structure of dimethyl sulfoxide−water mixtures and its influence on the solvation structure of solute *from a clustering point of view*, by means of a specially designed mass spectrometric system. It was observed that the propensity to the cluster formation is *nonlinearly* dependent on the solvent composition, exhibiting the existence of a critical value of mixing ratios where drastic changes in the microscopic solvent structure occur. It was also demonstrated that in such a solvent mixture the solvation structure of solutes such as 2-butanol, cyclopentanol, cyclohexanol, and phenol is greatly related to the microscopic solvent structures, implying that solute species interact with already established solvent clusters, rather than with individual solvent molecules.

Water−organic binary mixtures are powerful solvent systems frequently used,[1] because their chemical properties such as ionization power and hydrophobicity can be readily controlled by simply changing the mixing ratios. In these aqueous solvent mixtures, chemical reactions turn out to be greatly influenced by the solvent effect.[2] Frequently, solvent effects on chemical reactions shows a nonlinear dependence on the mixing ratios.[3] This is the result of the fact that the solvation shell around solutes departs from simple additive behavior with respect to the mixing ratios, which is complicated by the nature of the solvent structures,[4] together with the solute−solvent interactions.[5] Thus, it is mandatory to explore in detail the microscopic structure of the solvent mixtures, leading to a better understanding of how it affects the chemical processes occurring within the solvent mixtures.

A wealth of studies has centered on the characteristics of the microscopic structure of the water−dimethyl sulfoxide (DMSO) mixture, in which a wide variety of experimental and theoretical methods was employed, including neutron diffraction measurements,[6] thermodynamics,[7] NMR,[8] IR,[9] and molecular dynamics simulation.[10] It should be emphasized that the consistent picture emerging from these investigations is the presence of microheterogeneities, indicating cluster formation of like molecules (homologous association) within the solvent mixture. The existence of the microheterogeneity seems to be crucial properties of solvent mixture that entail the deviation from ideal mixing behavior. However, the microheterogeneity of the water−DMSO solvent mixture is still poorly characterized, owing to the lack of the direct ways of investigation. In this study, we made an attempt to characterize the microscopic solvent structure of aqueous DMSO and its influence on the preferential solvation of hydrophobic solutes, by measuring the changes in the degree of the cluster distribution as a function of the mixing ratio of binary mixtures. With this aim, here, we utilized a specially designed mass spectrometric technique that offers a direct way to isolate the clusters from solvent mixture. In recent papers,[11] we have demonstrated that this methodology can be successfully applied to illustrate the microscopic structure of solvent mixtures in terms of the clustering phenomenon that takes places in them.[12]

The details of the mass spectrometric technique used in this study have been provided elsewhere.[11] Sample solutions were directly introduced by the nozzle with a liquid chromatograph pump (Shimadzu, LC-10AD) at 0.08 mL/min. Generated liquid droplets underwent adiabatic expansion and fragmented into clusters. The resulting clusters were ionized by electron impact at 25 eV and analyzed by a quadrupole mass spectrometer (Extrel C50−4000). Four solutes (2-butanol, cyclopentanol, cyclohexanol, and phenol), obtained from Wako, Ltd., were used without further purification, and their mole fractions were kept low ($x = 0.002$). The 99.9% (HPLC grade; Wako, Ltd.) DMSO and Millipore Milli-Q filtered water were used for all experiments.

Figure 1 shows the mass spectra observed for DMSO−water mixtures taken at two different mixing ratios (mole fraction of water: X_w): (a) 0.97 and (b) 0.81. At $X_w = 0.97$, two major cluster series observed are water clusters, $(H_2O)_nH^+$, and their clusters interacting with one or two DMSO species such as $(DMSO)_1(H_2O)_nH^+$ or $(DMSO)_2(H_2O)_nH^+$. However, no self-associating DMSO clusters are observed in the mass spectrum, except for the DMSO dimer. In contrast, at $X_w = 0.81$, the DMSO clusters, $(DMSO)_m^+$, are predominantly shown, whereas the water clusters appear to be nearly suppressed despite the fact that the water concentration in these mixtures is about four times higher than the DMSO concentration. It is immediately apparent that there are changes in the microscopic solvent structure between two different solvent compositions.

The measurements of the mass spectra with varying X_w clearly indicated that the cluster structure was changed nonlinearly upon X_w, as shown in Figure 2. With decreasing water concentrations in these mixtures, the relative intensity of water clusters decreases slightly until the critical value for the water mole fraction around $X_w = 0.93$ is reached. At $X_w \approx 0.93$, the relative

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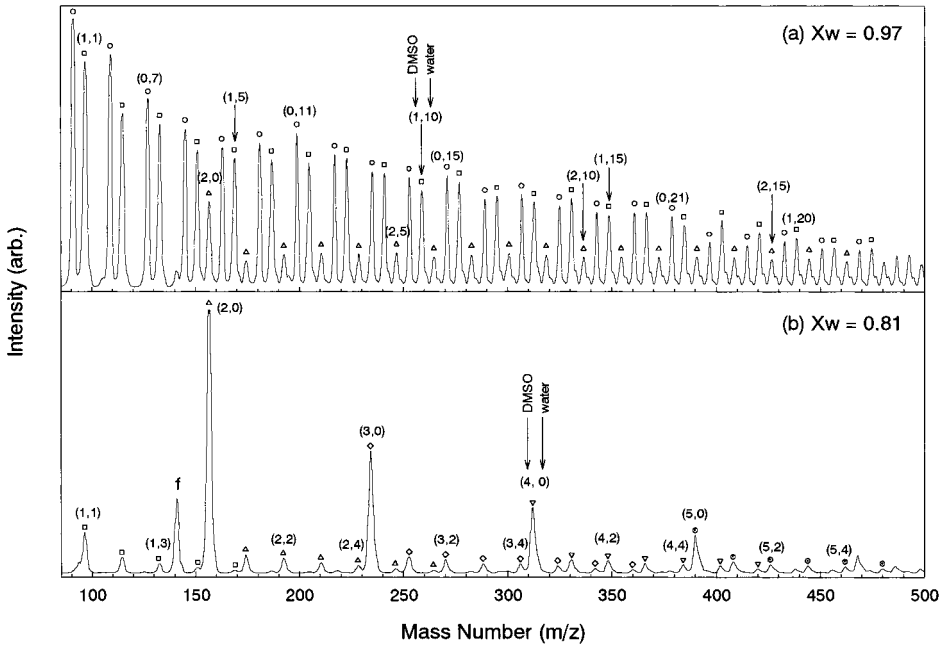

Figure 1. Typical mass spectra of DMSO−water binary solutions: (a) $X_w = 0.97$ and (b) 0.81, where X_w designates water mole fraction. The cluster ions $(DMSO)_m(H_2O)_nH^+$ are labeled as (m,n), where each peak is also represented by symbols according to the number of DMSO molecules, m. "*f*" in (b) designates the fragmentation peaks of DMSO clusters losing CH_3 group of DMSO.

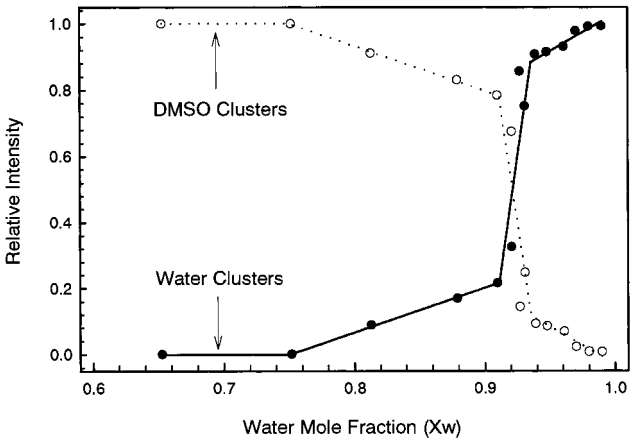

Figure 2. Observed variation of the intensity ratio $\sum(DMSO)_m/[\sum(DMSO)_m + \sum(water)_n]$ for DMSO clusters (open symbols and dotted lines) and $\sum(water)_n/[\sum(DMSO)_m + \sum(water)_n]$ for water clusters (closed symbols and solid lines), as a function of the water mole fraction (X_w), where $\sum(DMSO)_m$ and $\sum(water)_n$ represent the summed intensity of DMSO clusters, $(DMSO)_m^+$, and water clusters, $(H_2O)_nH^+$, within the mass range 80−500 amu, respectively.

intensity of the water cluster starts to drop suddenly and decreases down to 0.2 at $X_w \approx 0.91$. Thereafter, it begins to decrease again slowly and eventually becomes nearly zero beyond $X_w \approx 0.8$. The tendency for the DMSO clusters is opposite to that of the water clusters. This result manifests that the microscopic structure in DMSO−water mixtures varies *nonlinearly* with the solvent composition, exhibiting the existence of a critical value of the mixing ratios, at $X_w \approx 0.91-0.93$, where drastic changes in the microscopic structure occur.

On the basis of the result aforementioned, over the critical mixing ratio, DMSO exerts little, if any, effect on the water structure. Such a behavior may be explained by adopting the picture[7c,d] that DMSO tends to occupy cavities in the voluminous water structure without precluding the hydrogen-bonding network of water. Under these circumstances, DMSO is completely solvated by water clusters. The observation of a critical value at $X_w \approx 0.91-0.93$ is consistent, despite the totally different technique, with the NMR observation of the anomalous increase of motional freedom of water molecules only at $X_w \geq 0.90$,[8a] indicating that small amounts of DMSO do not perturb the overall hydrogen-bond network in water. In this way, our observation becomes reasonably amenable to explain a minimum value of the apparent molar volume of DMSO[7c,d] in aqueous solution around the critical value of the water concentration. This consequence supports the validity of the clustering phenomenon in solvent mixture as a sensitive probe of microscopic solvent structure.

Below the critical value, there might be no sufficient cavities in the water structure to accommodate added DMSO molecules in the mixtures. However, the change in the intensity of DMSO and water clusters is dramatic as compared to the small change in the mixing ratios. Upon decreasing the water mole fraction from 0.94 to 0.90, for example, the formation of DMSO clusters is greatly enhanced, whereas that of water clusters is significantly diminished (Figure 2). This might be attributed to two factors which accelerate the change in the microscopic clustering structures: hydrophobic interactions[13] among DMSO molecules in aqueous mixtures and the strength of the hydrogen bonds[10a,b] between water and DMSO species which is much stronger than that between water molecules.

In DMSO−water mixtures, we have examined the hydration behavior of hydrophobic solutes 2-butanol, cyclopentanol, cyclohexanol, and phenol. Figure 3 shows as an example the mass spectra of clusters obtained for DMSO−water mixtures with cyclopentanol as the solute at two different mixing ratios (X_w): (a) 0.97 and (b) 0.83. It exhibits a rather complicated pattern. Again the series of ion peaks corresponding to water, DMSO, and their mixed clusters are observed, similarly to DMSO−water mixtures without solutes. Besides, additional series of cluster ions are present such as the $(cyclopentanol)_x(DMSO)_m(H_2O)_nH^+$ cluster, in which the relative solvation pattern of the cyclopentanol molecule changes with mixing ratios. At high water concentration, for instance, the peaks of the form $(cyclopentanol)_x(H_2O)_nH^+$ clusters are only observed as shown in Figure 3a. This feature suggests a clear preference for water clusters to solvate the solute. As the water concentra-

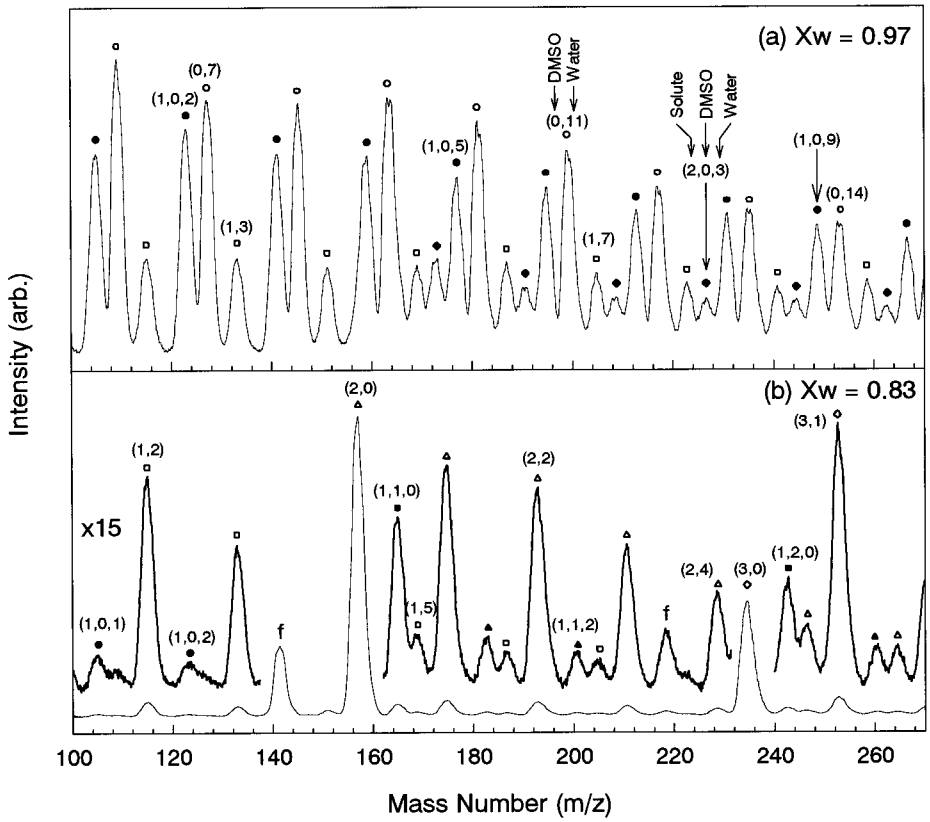

Figure 3. Typical mass spectra of DMSO−water mixtures in the presence of cyclopentanol as a solute: (a) $X_w = 0.97$ and (b) 0.83. The cluster ions corresponding to $(DMSO)_m(H_2O)_nH^+$ and $(cyclopentanol)_x(DMSO)_m(H_2O)_nH^+$ are labeled as (x,m,n) and (m,n), respectively, where each peak is also represented by symbols according to the number of DMSO molecules. The closed symbols refer to the cluster ions containing solute molecule. The other notations used are the same as in Figure 1.

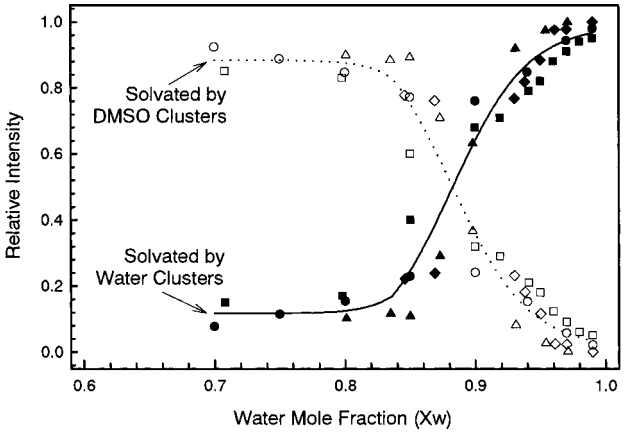

Figure 4. Intensity ratio of DMSO (open symbols and dotted line) and water (closed symbols and solid line) clusters solvating solute, $\sum(\text{solute})(\text{solvent})/[\sum(\text{solute})(\text{DMSO})_m + \sum(\text{solute})(\text{water})_n]$, against X_w, in the mass range of 80−500 amu: 2-butanol (diamond), cyclopentanol (triangle), cyclohexanol (circle), and phenol (square), where "(solvent)" corresponds either to $(DMSO)_m$ or $(water)_n$. The other notations used are the same as in Figure 2.

tion decreases, it is found that the solvation propensity of cyclopentanol molecule switches from water to DMSO clusters, leading to the preferential formation of clusters of the form $(cyclopentanol)_x(DMSO)_mH^+$. As exhibited in Figure 3b, DMSO clusters appear to preferentially surround cyclopentanol solute, whereas the solvation of cyclopentanol by water clusters is relatively suppressed.

Details on the solvation behavior of the solutes are illustrated in Figure 4, which should be compared with the microscopic clustering structure in the DMSO−water mixtures as seen in Figure 2. The solvation structure of all solutes employed in this study shows nearly the same characteristics, irrespective of the nature of the solutes.[14] At high water mole fraction over $X_w \approx 0.90$, the solute is preferentially solvated by water clusters, whereas below $X_w \approx 0.90$, it is preferentially solvated by DMSO clusters. Our result on the solvation trend of phenol is in keeping with previous NMR studies, which showed that phenol is preferentially solvated by DMSO below $X_w = 0.90$.[8c] It is obvious that the solvation structure of the solutes is found to be also *nonlinearly* sensitive to the mixing ratios of DMSO−water mixtures, like the microscopic solvent structure of the DMSO−water mixture in Figure 2. The experimental observations shown in Figures 2 and 4 indicate that the factor governing solvation structure of solutes is immediately related to microscopic solvent structures found for the DMSO−water mixtures. As a consequence, the nature of the preferential solvation should be originated from the propensity that solute species dissolved in a water−DMSO solvent mixture interact with already established solvent clusters, rather than individual solvent molecules.

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(12) In this method, the clusters are isolated (or extracted) from liquid droplets injected into the vacuum chamber, where the liquid droplets are fragmented into clusters through adiabatic expansion. Even though the weakly interacting molecules are vaporized from the liquid droplets, the strongly interacting molecules remain in the clusters generated through the fragmentation of the liquid droplets. Accordingly, the observed cluster structure is related to the intermolecular interactions in solution.

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(14) Generally alcohol is quite similar to water in its ability to serve as both proton donor and acceptor. However, phenol acts primarily as a proton donor because of its more acidic character in water and its hydrates depart from water-like behavior when there are sufficient water molecules to interact with phenol.[15] The Gibbs free energy of solvation of phenol in water ($\Delta G_{sol} = -6.6$ kcal/mol) is larger than that of alcohol (for example, $\Delta G_{sol} = -4.5$ kcal/mol for 2-butanol), where the solvation energies gradually decreases with increasing number of carbons in alcohols.[16] The heat of solution of phenol in DMSO ($\Delta H_{sol} = -0.7$ kcal/mol) is larger than that in water ($\Delta H_{sol} = +2.7$ kcal/mol).[17]

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